CHEMICAL DEPLETION OF LOWER STRATOSPHERIC OZONE

IN THE 1992-1993 NORTHERN WINTER VORTEX

G. L. Manney, L. Froidevaux, J. W. Waters, R. W. Zurek,

W. G. Read, L. S. Elson,

Jet Propulsion Laboratory/California Institute of Technology,

J. B. Kumer, J. L. Mergenthaler, A. E. Roche,

Lockheed Palo Alto Research Laboratory,

A. O'Neil],

Centre for Global Atmospheric Modelling, Reading UK,

R. S. Harwood, 1. MacKenzie,

Edinburgh University, Edinburgh UK,

R. Swinbank,

Meteorological Office, Bracknell UK

Satellite observations of ozone and chlorine monoxide in the Arctic lower stratosphere during winter 1992-1993 are compared with observations during other winters, observations of long-lived tracers and the evolution of the polar vortex. Chlorine in the lower stratospheric vortex during February 1993 was mostly in chemically reactive forms. The observed decrease in lower stratospheric ozone during February and early March 1993 appears consistent with chemical destruction by this reactive chlorine, and is inconsistent with changes caused by transport processes alone.

MLS observations of ozone and ClO during the 1992-1993 northern winter, and their relation to the evolution of the stratospheric polar vortex, are compared with those in the 1991-1992 northern and 1992 southern winters. MLS observations are also compared to Nimbus 7 Limb Infrared Monitor of the Stratosphere (LIMS) ozone during the 1978-1979 Arctic winter, when ozone depletion by chlorine chemistry in the lower stratosphere was not expected. N_2O and CH_4, measured by the Cryogenic Limb Array Etalon Spectrometer (CLAES) instrument on board UARS, are used to examine transport effects.

Lower stratospheric temperatures in 1991-1992 rose above the PSC formation threshold in late January, due to a strong stratospheric warming[13,17]; ClO abundances were observed to decrease after this time[7-10]. Analyses of aircraft and ground-based observations[18,19,20] showed decreasing ozone in the lower stratosphere (=15-19 km) in January 1992; MLS observations[10] showed vortex-averaged ozone decreasing during its north-viewing period in early January 1992 on the 465 K ($\approx$19 km) isentropic surface. More detailed comparison here of MLS observed changes in ozone with variations expected to be caused by transport during January and February 1992 adds to the evidence that lower stratospheric ozone in January 1992 was depleted by chlorine chemistry.

In 1992-1993 the MLS measured enhanced ClO in the Arctic polar vortex beginning in early December 1992; by mid-February, the Arctic vortex was nearly filled with ClO > 1ppbv[10] which persisted until the end of February, Vortex-averaged MLS ozone at 465 K was observed to decrease by $\approx$20% between mid-February and mid-March. Analyses of long-lived tracer data and vortex evolution show that this decrease in ozone was inconsistent with changes that could be caused solely by transport processes at this time. These results indicate significant depletion of ozone by chlorine chemistry in the Arctic lower stratospheric vortex between mid-February and mid-March 1993.

For consistency, UKMO temperatures are used to interpolate gridded MLS and CLAES data from pressure to isentropic surfaces.

Ozone in the Arctic Vortex

Figure 1 shows maps of ozone at 465 K ($\approx$19 km) in mid-February android-March for three Arctic winters, along with several PV contours. Much variability in the size and shape of the vortex is apparent. During 1979 and 1993, the vortex is considerably smaller in mid-March than in mid-February, because strong stratospheric warmings have eroded it. No strong warmings occur in late winter in 1992, and the size of the vortex does not change much. Ozone in the vortex decreased between mid-February and mid-March 1993, in contrast to increases during this period in 1979 and 1992. Ozone mixing ratios peak in the mid-stratosphere, near $\approx$35 km at high latitudes. Thus, downward transport across isentropic surfaces, expected due to diabatic cooling in the polar winter stratosphere, should increase ozone at 465 K. Horizontal transport, however, could decrease vortex ozone since below $\approx$550 K ($\approx$21 km), there is less ozone at low latitudes than in the polar vortex,

There is no obvious evidence of low latitude air being entrained into the vortex in 1993, as shown in Figure 2, The sequence of **465** K ozone maps in February and March 1993 shows the decrease in vortex ozone to be fairly uniform in time, with no sign of comparatively ozone poor low latitude air entering the vortex. Some ozone rich air is, however, observed being drawn off the edge of the vortex. This could decrease ozone in the vortex only if downward transport of higher ozone was insufficient to replenish it; it will be shown in the following sections that this is not the case.

Figure 3 highlights the observed evolution of ozone, ClO, and lower stratospheric temperatures in the vortex for the three Arctic winters. Vortex-averaged ozone is shown in the mid-stratosphere (840 K, $\approx$32 km) and vortex-averaged ozone, vortex minimum

vortex edge. In 1992 a strong stratospheric warming began in mid-January when MLS switched to looking south; a steep increase in ozone is seen prior to this switch. Ozone at 840 K increases slowly from mid-February to mid-March 1992, consistent with weaker poleward and downward transport during this relatively quiescent time. In 1993 the 840 K ozone increases most rapidly from mid-February to mid-March, during strong warmings. In each year, the behavior in the mid-stratospheric vortex, where chlorine chemistry is expected to be unimportant, is consistent with that expected from transport processes.

The behavior of LIMS ozone in 1978-1979 in the lower stratosphere is thought to represent dynamical changes, since levels of stratospheric chlorine were lower by $\approx 70\%$ than at present and the 1978-1979 Arctic winter was particularly warm. The 1978-1979" data at 465 K show a decrease in ozone for a few days in late January, followed by a rapid increase that appears qualitatively consistent with enhanced descent during the stratospheric warmings. Since the lower stratospheric vortex is weaker during 1978-1979, ozone is less confined in the vortex and less strongly correlated with PV. During times of strong wave activity the strongest diabatic descent is at the periphery of the vortex[28], leading to higher ozone there rather than in the vortex interior (e.g., Fig. 1a). When highest ozone is near the outside edge of the vortex it is not included in the average shown in Fig 3b. During periods of strong wave activity, intrusions of low-latitude, ozone poor air into the vortex may also occur[29].

The preceding discussion of ozone evolution at 840 K and in 1978-1979 at 465 K illustrates the wide variety of behavior possible during the Arctic winter due solely to dynamics. The behavior of ozone in the Arctic lower stratosphere in recent years is expected to exhibit variations caused by both dynamical and chemical processes, due to large abundances of stratospheric chlorine.

MLS observed enhanced ClO in the polar vortex at 465 K from late December 1991 to mid-January 1992 (Fig. 3d), during the time of low temperatures [0] (Fig. 3c). By mid-February when MLS looked north again, C1O had decreased substantially and continued

and September 199230'3 [1], where vortex-averaged ozone at 465 K decreased at= 1.4% per day. Vortex-averaged ClO mixing ratios in the Antarctic in mid-August 1992 were comparable to mid-February 1993 Arctic values, but the duration of enhanced ClO in the Arctic was shorter[10,30]. Based on calculations like those done for January 199210 using MLS ClO, the expected vortex-averaged ozone loss over the Feb/Mar 1993 time period is ≈0.9% per day. This calculation is quantitatively consistent with the observations, particularly since ozone should increase in absence of chemical depletion.

Separation of Chemical and Dynamical Effects

The observations of enhanced ClO suggest that the 465 K Arctic ozone changes during early January 1992 and late winter 1993 are not caused solely by dynamics. It is not possible from the area] averages in Fig. 3 to unambiguously distinguish between dynamical and chemical effects. As was clearly demonstrated during the 1978-1979 winter, a number of dynamical processes, both diabatic and adiabatic, can affect the distribution of ozone on an isentropic surface[32] and hence increase or decrease the average shown in Fig, 3. Below we examine the behavior of ozone in relation to that of passive tracers to separate chemical and dynamical effects.

The Arctic vortex is so distorted and variable (Fig. 1) that zonal means obscure details of the flow, and average together values from inside and outside the vortex. An average more useful for diagnostic purposes is obtained by changing coordinates from latitude to PV[72,33,34], and averaging around a PV contour. Changes in the mixing ratio at constant PV and θ provide information on diabatic and chemical processes[32,35]. Figure 4 shows time series of N_2O from CLAES on the 465 K isentrope, averaged around PV contours for the northern hemisphere late winters of 1991-1992 and 1992-1993, and the southern hemisphere late winter of 1992. The region of strongest PV gradients that identifies the edge of the polar vortex is generally between 1.0 and 1.4 x 10-4 s] in the

vortex. Comparison with dynamical changes expected from examination of N_2O (Fig. 4b) indicates that the observed ozone evolution is inconsistent with the effects of transport alone, as expected from simultaneous MLS observations of greatly enhanced ClO during this period. This is direct observational evidence for chemical ozone depletion in the Arctic lower stratosphere during Feb/Mar 1993.

Figure 6 compares the vertical extent of the observed enhancement in ClO with" changes in ozone during late winter. Changes in ozone averaged around PV contours are plotted as a function of PV and θ, along with the time-average ClO observed by MLS during late winter. The thick black line indicates the approximate edge of the vortex, The 1979 ozone (Fig. 6a) shows behavior expected for no chemical loss during a dynamically active period: a large increase inside the polar vortex throughout the lower stratosphere. The plots for 1992 in the Antarctic (Fig. 6f and 6g) show the behavior expected when chemical loss dominates: ozone decreases below ≈ 650 K (≈ 27 km) throughout the vortex, coincident with the region of enhanced ClO.

ClO in the Arctic lower stratosphere during Feb/Mar 1992 is low compared with that observed when temperatures are low enough for PSC formation. Ozone in Feb/Mar 1992 below about 650 K increased slightly inside the vortex, consistent with weak diabatic descent at this time. An ozone decrease of $\approx 10\%$ occurs in 1992 between 600 and 700 K at highest PV values; a decrease of $\approx 7\%$ is seen in this region in 1993. The decrease in 1992 occurs mainly between 10 and 21 March, and is accompanied by a larger increase in NO_2 (from CLAES) and ClO (from MLS) in March 1992 than in March 1993. First-order estimates of gas-phase reactions involving these species suggest that this could lead to more ozone destruction near 650 K in 1992 than in 1993, as observed.

In 1993 enhanced Arctic ClO extends to near the vortex edge, as in the south, but the vertical extent in the Arctic is less, extending only up to ≈ 580 K. Although Arctic ClO abundances in mid-February 1993 are comparable to Antarctic values in mid-August

Arctic lower stratospheric temperatures were low enough for PSC formation for approximately 1 month during 1991-1992[10,*,3], ending in late January. They were low enough for nearly 2 months during 1992-1993, until near the end of February, when more sunlight reaches the polar regions and sustains the ozone destruction cycle over larger areas. This year (1993- 1994), Arctic lower stratospheric temperatures were sporadically y below the PSC formation threshold in December 1993, and continuously slightly below it from early January through early February; MLS measured some enhancement of ClO in the Arctic vortex in early February 1994. The Arctic lower stratosphere in the past 15 years has been sufficient y cold for PSC formation for as long as 2 1/2 months, and as late as mid-March[15]. It is expected, therefore, that there will be years in the near future, while stratospheric chlorine levels continue to increase, when ozone depletion in the Arctic lower stratosphere will equal or exceed that in 1993, Since the Arctic polar vortex is weaker and more variable than the Antarctic, air that becomes depleted in ozone in the polar regions can be more readily transported to mid-latitudes during winter in the Arctic[38]. Vortex processes may thus be of significance to recent decreases in ozone observed during winter at northern mid-latitudes[39,40,41]

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Figure Captions

FIG. 1 Ozone cm the 465 K isentropic surface in mid-February and mid-March 1979, 1992, and 1993. Potential vorticity contours of 2.5, 3.0 and 3.5 x 10-5 K $m^2kg^{-1}s^{-1}$ are overlaid in black; these values are in the region of strong PV gradients that identifies the polar vortex edge. The projection is orthographic, extending to the equator; thin dashed circles show 30^oN and 60^oN latitudes.

FIG. 2 Ozone on the 465 K isentropic surface at 4 day intervals from 18 February through 10 March 1993. Potential vorticity contours and layout are as in Fig. 1.

FIG. 3 (a), (b), and (d) Vortex-averaged mixing ratios, calculated by dividing the area integral of the mixing ratio inside a PV contour (at 465 K, the outermost contour in Fig. 1 and Fig. 2 is used), by the area enclosed by the contour, of ozone (ppmv) at 840 K (a) and 465 K (b), and CIO (ppbv) at 465 K (d), for three northern winters; (c) minimum 465 K temperatures in the same region as used for the vortex averages. Red line shows the 1978-1979 winter (from LIMS data), and the green and blue lines show the 1991-1992 and 1992-1993 winters, respectively (from MLS data for ozone and C1O, and UKMO data for temperatures). The gaps in MLS data are when the instrument is observing the southern hemisphere.

FIG. 4 Time series of CLAES $N_2$0 mixing ratios (ppbv), averaged around a PV contour, as a function of PV, for 9 Feb (1 1 Aug) through 20 Mar (19 Sep) in the northern hemisphere (southern hemisphere). The absolute value of PV is used in the southern hemisphere. PV is scaled in "vorticity units", where it is divided by a standard atmosphere value of the static stability[13,42], and thus has units of vorticity (s'). With this scaling, PV on isentropic surfaces throughout the stratosphere has a similar range of values. The

465 K OZONE

(a)

1979
(LIMS)

11 Feb

(b)

17 Mar

(c)

1992
(MLS)

16 Feb

(d)

21 Mar

(e)

1993
(MLS)

11 Feb

(f)

17 Mar

1.8   ozone (ppmv)   3.4
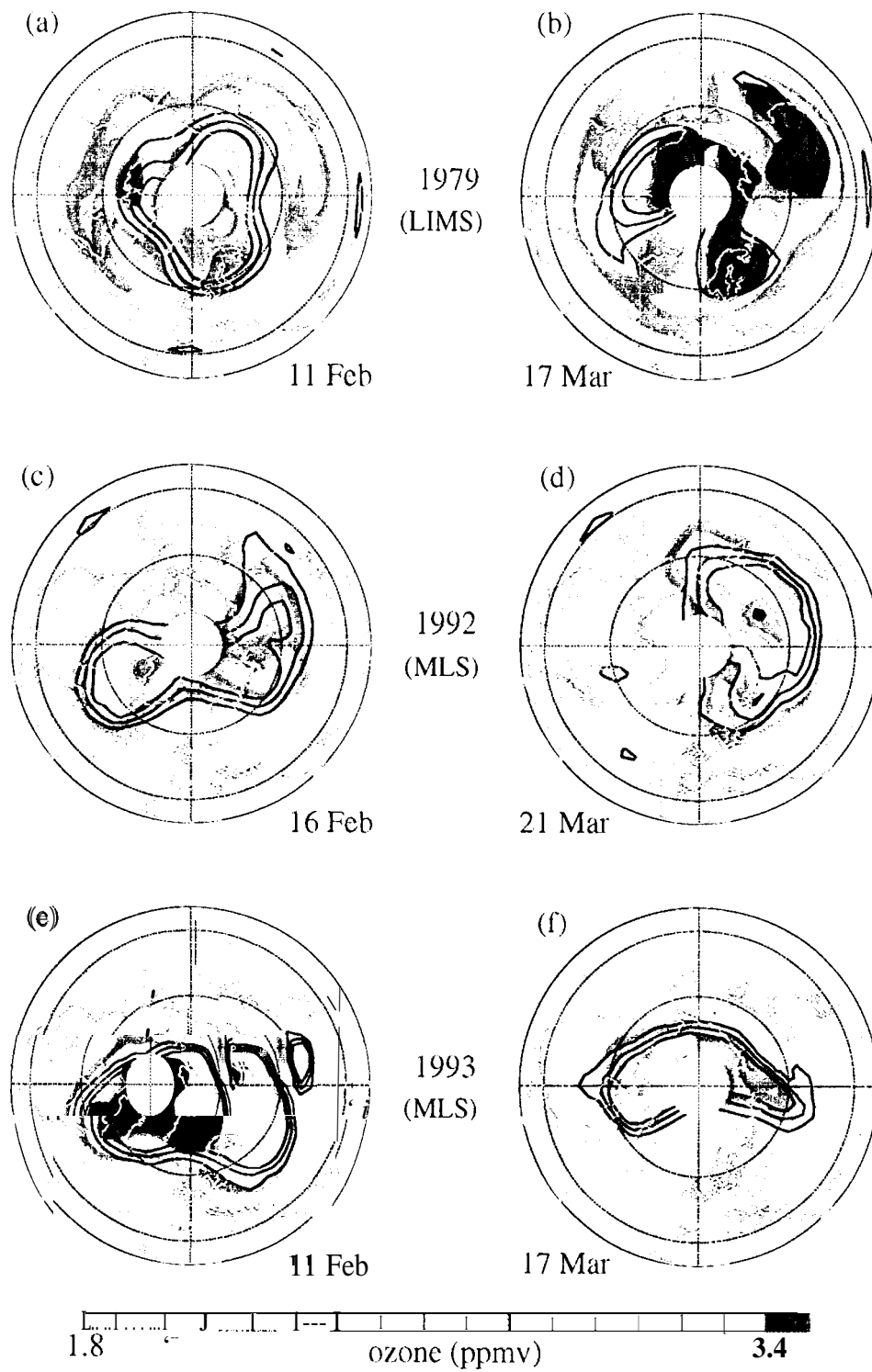
Figure 1

465 K MIS OZONE 1993

(a)
18 Feb

(b)
22 Feb

(c)
26 Feb

(d)
2 Mar

(e)
6 Mar

(f)
10 Mar

ozone (ppmv)

1.8   3.4

Figure 2

(a) 840 K ozone (ppmv) .

(b) 465 K ozone (ppmv)

(c) 465 K minimum T (K)

(d) 465 K ClO (ppbv)

1 Jan   1 Feb 1 Mar

——————— 1978-1979 (l.] MS)

—————————]991 - 1992 (MLS & UKMO)

——————— 1992-1993 (MLS & UKMO)

Figure 3

NH 1992

NH 1993

Potential Vorticity $)^{4}$ 1/s)

9 Feb   1 Mar

SH 1992

11   Aug 1 Sep

4()

465 K N_2O (ppbv)

280

Figure 4

(a) NH 1978-1979 (LIMS)

(b) NH 1991-1992 (MLS)

Potential Vorticity $(10^{-4}$ 1/s)

(c) NH 1992-1993 (MLS)

1 Dec   1 Jan   1 Feb   1 Mar

(d) SH 1992 (MLS)

1 Jun   1 Jul   1 Aug   1 Sep

0.8   3.4

465 K ozone (ppmv)

Figure 5

(a) *17* Mar -10 Feb 1979 NH

Figure 6

(b) 21 Mar - 15 Feb 1992 NH

(c) 15 Feb to 21 Mar 1992 NH

(d) 17 Mar - 10 Feb 1993 NH

(e) 10 Feb to 17 Mar 1993 NH

(f) 18 Sep -14 Aug 1992 SH

(g) 14 Aug m 18 Sep 1992 SH

potential vorticity (10^4 1/s)

potential vorticity (10^{-4} 1/s)

-1   1

Ozone Change (ppmv)

()   1.5

Average ClO (ppbv)